

PATENT COOPERATION TREATY

PCT

NOTICE INFORMING THE APPLICANT OF THE
COMMUNICATION OF THE INTERNATIONAL
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

DE GREGORI, Antonella
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ITALIE

Date of mailing (day/month/year) 09 December 1999 (09.12.99)		
Applicant's or agent's file reference 75153		
International application No. PCT/EP99/01821	International filing date (day/month/year) 18 February 1999 (18.02.99)	Priority date (day/month/year) 04 June 1998 (04.06.98)
Applicant ENITECNOLOGIE S.P.A. et al	IMPORTANT NOTICE	

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
AU,CN,EP,IL,JP,KP,KR,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:
AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CU,CZ,DE,DK,EA,EE,ES,FI,GB,GD,GE,GH,GM,HR,HU,
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The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on
09 December 1999 (09.12.99) under No. WO 99/63340

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a **demand for international preliminary examination** must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the **national phase**, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

20. DIC. 1999
Int. PCT/EP99/01821

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 740.14.35	Authorized officer J. Zahra Telephone No. (41-22) 338.83.38
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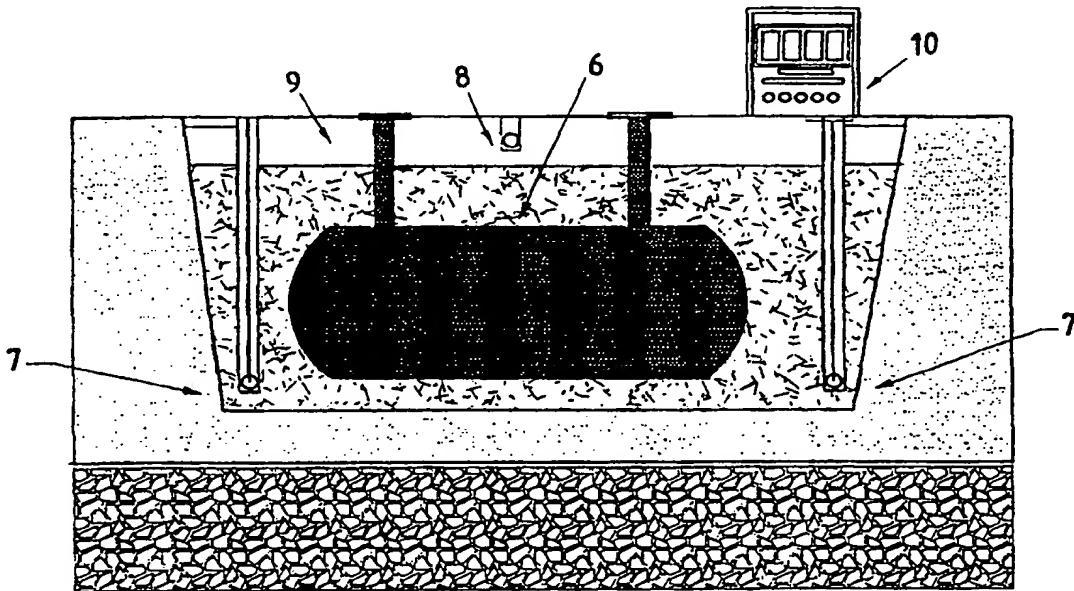
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : G01N 33/24, 33/00, 27/12		A1	(11) International Publication Number: WO 99/63340 (43) International Publication Date: 9 December 1999 (09.12.99)
(21) International Application Number: PCT/EP99/01821 (22) International Filing Date: 18 February 1999 (18.02.99) (30) Priority Data: MI98A001248 4 June 1998 (04.06.98) IT		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(71) Applicant (for all designated States except US): ENITEC-NOLOGIE S.P.A. [IT/IT]; Via Felice Maritano, 26, I-20097 San Donato Milanese (IT). (72) Inventor; and (75) Inventor/Applicant (for US only): DE ANGELIS, Lucio [IT/IT]; Via San Giovanni Bosco, 49, I-00175 Rome (IT).		Published <i>With international search report.</i>	
(74) Agents: DE GREGORI, Antonella et al.; Ing. Barzano' & Zanardo, Milano S.p.A., Via Borgonuovo, 10, I-20121 Milan (IT).			

(54) Title: PROCESS FOR THE DETERMINATION OF MTBE IN THE GROUND AND AIR



(57) Abstract

A process is described, and also the system for its embodiment, for the determination of pollution by MTBE in the soil. An example is described relating to the monitoring of underground fuel tanks for autotraction containing this oxygenated additive.

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PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

DE GREGORI, Antonella et al.
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PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing (day/month/year)	15.02.2000
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Applicant's or agent's file reference 75153	IMPORTANT NOTIFICATION	
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International application No. PCT/EP99/01821	International filing date (day/month/year) 18/02/1999	Priority date (day/month/year) 04/06/1998
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Applicant ENITECNOLOGIE S.P.A. et al.
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1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

17. FEB. 2000

Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Danti, B Tel. +49 89 2399-8577	
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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 75153	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP99/01821	International filing date (day/month/year) 18/02/1999	Priority date (day/month/year) 04/06/1998
International Patent Classification (IPC) or national classification and IPC G01N33/24		
<p>Applicant ENITECNOLOGIE S.P.A. et al.</p>		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input checked="" type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application 		
Date of submission of the demand 17/11/1999	Date of completion of this report 15.02.2000	
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	<p>Authorized officer Goetz, M</p> <p>Telephone No. +49 89 2399 8697</p> 	

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP99/01821

I. Basis of the report

1. This report has been drawn on the basis of (substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.):

Description, pages:

1-8 as originally filed

Claims, No.:

1-4 as originally filed

Drawings, sheets:

1/4-4/4 as originally filed

2. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

3. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP99/01821

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims 1 - 4
	No:	Claims
Inventive step (IS)	Yes:	Claims 1 - 4
	No:	Claims
Industrial applicability (IA)	Yes:	Claims 1 - 4
	No:	Claims

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

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INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET

International application No. PCT/EP99/01821

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. In the light of the available prior art, the subject-matter of present claims 1 - 4 is novel and involves an inventive step.

Desimas et al., Advances in Instrumentation and Control 45/1, 1990, pages 451 - 461, relates to the determination of MTBE using spectroscopic means. There is no mention of another measuring method.

US-A-4 631 952 and **US-A-5 514 338** describe sensors for detecting volatile organic compounds such as MTBE; the sensors do not have a sensitive element made of a semi-conductor metal oxide containing platinum, neither are they equipped with a heating element.

Apart from the differences in sensor elements to be used, the above documents do not suggest the particular combination of two sensors as recited in the present process and device of claims 1 - 4, wherein the first sensor is located in the earth and the second one in the air just above ground level.

2. Claims 1 - 4 therefore meet the requirements according to Art. 33(2) - (4) PCT.

Re Item VII

Certain defects in the international application

1. It appears that lines 14 and 15 of claim 1 should read "... range of 300 to 500°C ..." instead of "... range of 300 and 500°C ...".
2. The unit of measure "micron" employed in claim 3 and on page 3 of the description is not additionally expressed in terms of the units stipulated by Rule 10.1(a) PCT.

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PATENT COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 75153	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/EP 99/01821	International filing date (day/month/year) 18/02/1999	(Earliest) Priority Date (day/month/year) 04/06/1998
Applicant ENITECHNOLOGIE S.P.A. et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

contained in the international application in written form.

filed together with the international application in computer readable form.

furnished subsequently to this Authority in written form.

furnished subsequently to this Authority in computer readable form.

the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. **Certain claims were found unsearchable** (See Box I).

3. **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

the text is approved as submitted by the applicant.

the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

the text is approved as submitted by the applicant.

the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

as suggested by the applicant.

because the applicant failed to suggest a figure.

because this figure better characterizes the invention.

2

None of the figures.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/01821

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G01N33/24 G01N33/00 G01N27/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DESIMAS B ET AL: "MEASUREMENT OF MTBE IN GASOLINES BY NIR" ADVANCES IN INSTRUMENTATION AND CONTROL, vol. 45, no. PART 01, 1 January 1990 (1990-01-01), pages 451-461, XP000172009 ISSN: 1054-0032 the whole document ---	1-4
A	US 4 631 952 A (DONAGHEY LEE F) 30 December 1986 (1986-12-30) column 3, line 66 - column 10, line 55; figures ---	1-4
A	US 5 514 338 A (SIMON MORRIS ET AL) 7 May 1996 (1996-05-07) column 3, line 10 - column 5, line 5; figures -----	1-4



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the International search report

20 July 1999

28/07/1999

Name and mailing address of the ISA

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Bosma, R

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/01821

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4631952	A 30-12-1986	NONE	
US 5514338	A 07-05-1996	NONE	

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601N33/88

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0065-2814/90/451-461/\$0 + .50pp



XP 000172009

E MEASUREMENT OF MTBE IN GASOLINES BY NIR

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ABSTRACT

The use and measurement of methyl tertiary butyl ether (MTBE) in gasolines is increasing in importance to the oil refining industry. Remote single strand fiber optic spectroscopy provides unique advantages over currently implemented techniques. Such advantages include: accurate results in less than 30 seconds, remote distances of over 50 meters from analyzer to sample point, and no sample preparation. MTBE in the range 0-16 volume % may be measured through Second Overtone Near Infrared (SONIR) spectrophotometry and multivariate calibrations with an associated standard error of prediction of 0.121 volume % MTBE. This technique introduces the potential for on-line applications in oil refineries and field checking capabilities for regulatory agencies.

KEY TERMS

NIR : Near Infrared
SONIR : Second Overtone Near Infrared
PLS : Partial Least Squares
SEE : Standard Error of Estimate
SEP : Standard Error of Prediction
MTBE : Methyl Tertiary Butyl Ether

INTRODUCTION

In recent years the U.S. gasoline pool has been undergoing multiple changes. These changes include: higher octane products, lead phasedown, and lower Reid Vapor Pressure (RVP) products. As a result, MTBE is gaining widespread appeal with refiners as a gasoline blending component for both premium and regular grade gasolines. This is due to its high octane and moderate volatility properties without adversely impacting drivability. The currently accepted technique for measuring MTBE is the "Standard Test Method for Determination of C₁-C₄ Alcohols and MTBE in Gasolines by Gas Chromatography" (ASTM D4815¹), where MTBE is determined in the concentration range 0.1 to 10.0 volume percent. Precision statistics associated with this method are: reproducibility = 24% and repeatability = 10% as defined by ASTM criteria¹. NIR fiber optic spectrophotometry with multivariate calibration provides a rapid and reliable alternative to the gas chromatographic determination of MTBE in gasolines.

Partial least squares (PLS) is the multivariate calibration technique used throughout this paper. PLS permits multivariate calibration of NIR analyzers by mathematically recording a calibration model. A PLS model contains correlation information from two matrices. In this application the two matrices are: 1) a set of spectra and 2) a set of corresponding MTBE concentrations. Once a model is generated, spectra are used as input data in model computations of MTBE. The premise for using SONIR data in modeling MTBE, is the spectral bands which are characteristic of MTBE. The internal oxygen present in MTBE significantly changes the location of the second C-H overtones relative to the C-H overtones from

methyl groups attached to primary and tertiary carbons in analog compounds that do not contain oxygen.

EXPERIMENTAL

Spectra from 74 samples were used in generating PLS models to predict volume percentages of MTBE. The spectra were recorded in the range 900-1600 nm by a double beam scanning fiber optic spectrophotometer controlled by a remote host computer (see figure 1). Two sets of spectra (lab and field) were obtained by using 112 meters of single strand 500 micron fiber optic cable with a total of three coupling points post instrument. One point of fiber coupling occurred at the instrument/sample interface which was accomplished through a transmission probe assembly specifically designed to utilize 1 cm cuvettes (see figure 2). The other two points of coupling occurred in fiber runs: one in the transmitting and one in the receiving fiber. Spectra were recorded against an air reference using 4 scan averaging at 23°C. A total of 226 wavelengths (1100-1550 nm in even increments) were selected for PLS modeling of MTBE. The 1100-1300 nm region contains the second overtones from symmetric and asymmetric methyl, methylene, methine, aromatic, and olefinic C-H stretches. The 1350-1500 nm region contains absorption bands which result from combinations of stretching and bending modes from methylene, methine, aromatic, and olefinic C-H bonds⁽²⁾. Data pre-treatment consisted of two 17 point Savitzky-Golay smooths and baseline correction at 970 nm. This method is very similar to that used in the NIR determination of octane number in gasolines by PLS⁽³⁾.

LABORATORY SAMPLES FOR PLS CALIBRATION

1, 2, 4, 9, 12, and 16 volume % MTBE additions were made to three grades (84, 87, and 91 R+M/2) of unleaded gasoline from a single vendor. These 21 (18 with MTBE added and 3 neat) laboratory samples were used in the preliminary evaluation of the relationship between the SONIR spectra and the volume % MTBE present in each fuel. The SEE from a 4 factor PLS model is 0.092 volume % MTBE calculated from (1).

$$SEE = \left[\sum_{j=1}^n (y_{j,a} - y_{j,p})^2 / (n-1) \right]^{1/2} \quad (1)$$

where: n = number of samples in calibration.
j = sample number
 $y_{j,a}$ = actual value.
 $y_{j,p}$ = predicted value.

An estimate of the SEP (see equation 2) from this modeling was obtained by validation. This was accomplished by removing a minimum of one sample and a maximum of three from the data set, and generating eight 4 factor models from the balance of spectra in each case. From this set of 21 prediction results, the SEP is 0.121 volume % MTBE.

$$SEP = \left[\sum_{j=1}^n (y_{j,a} - y_{j,p})^2 / (n-1) \right]^{1/2} \quad (2)$$

where: n = number of samples in predictions.
j = sample number
 $y_{j,a}$ = actual value.
 $y_{j,p}$ = predicted value.

Figure 3 gives a plot of the actual volume % MTBE against the predicted volume % MTBE used to determine the SEP from the laboratory samples. This laboratory work provides an estimate of the errors associated with instrumental/PLS system. The ability to effectively determine MTBE in gasolines using laboratory samples motivated further investigation of PLS modeling using spectra from field samples and volume % MTBE obtained by current ASTM methodology⁽¹⁾.

FIELD SAMPLES

Three sets of samples were selected which represent premium, regular unleaded and regular leaded fuels from eight major vendors. The volume % MTBE as determined by Saybolt Laboratories⁽⁴⁾, was in the following ranges: 1) 18 samples with 0.0 % 2) 19 samples with 13.3-15.0 % and 3) 16 samples with 9.7-12.9 % MTBE. One sample from the third set (9.7-12.9%) was sent to Saybolt in duplicate to examine the repeatability of the ASTM method, where the volume % MTBE was reported as 10.1 and 11.2. These results are within and typical of the ASTM repeatability statistics from the gas chromatographic method. Both samples and their corresponding reported values were included in subsequent calibrations. The SONIR prediction results for the duplicate samples are 10.0 and 10.7. The trends from the gas chromatographic and SONIR analysis using the duplicate samples are similar. Since the SONIR results from the duplicate samples produced a deviation far greater than expected from the SEP determined using the lab samples, there is an indication that the two samples may not be true duplicates.

The 21 samples from the laboratory set were added to the field samples to give a total of 74 samples for evaluation. The SEE from a 6 factor PLS model is 0.8 volume % MTBE calculated from (1). An estimate of the SEP (see equation 2) from this modeling was obtained by removing a minimum of 6 samples and a maximum of 14 from the data set, and generating eight 6 factor models from the balance of spectra. From the set of 74 prediction results, the SEP is 1.1 volume % MTBE. Figure 4 gives a plot of the actual volume % MTBE against the predicted volume % MTBE used to determine the SEP from the field samples. Due to the distribution of MTBE concentrations normally encountered in the field (either in the 12 % range or no MTBE), a sub-set was selected for calibration where the set of samples containing no MTBE (called the nil set) was removed. An estimate of the SEP from the sub-set modeling was obtained by removing a minimum of 7 samples and a maximum of 14 from the data set, and generating five 6 factor models from the balance of spectra. From the set of 56 prediction results, the SEP is 0.7 volume % spectra. Figure 5 gives a plot of the actual volume % MTBE against the predicted volume % MTBE from predictions using this sub-set. This was done in an attempt to illustrate the modeling capabilities of this method without being limited by a poorly distributed population of data.

A summary of the results obtained from the three sets evaluated is shown in table 1.

Table 1
Comparison of Results Using Various Data Sets

Data Set	Factors Used	SEE	SEP
Lab	4	0.092	0.121
Field + Lab	6	0.8	1.1
Field + Lab*	6	0.6	0.7

* The nil set from the field + lab samples were removed for this analysis.

The total number of factors used to predict volume % MTBE increased from 4 to 6 when field samples were included. This was due to the increase in compositional variations of the base gasolines from the different vendors (as indicated by the scores statistics from the PLS model).

Notice that the errors in the predictions from the field set are larger than the errors in the predictions from the laboratory set. This is because the errors in the data from the field reference method (by gas chromatography) exceed those of the data from the laboratory reference method (by gravimetric addition). The errors associated with the concentrations of the standards used for calibration ultimately limit the prediction results from modeling of such referee data.

THE EFFECTS OF VARIABLE FIBER LENGTHS

The fiber optics used in this experiment exhibited a silanol absorption band^[5] at 1385 nm of approximately 1 absorbance unit per 100-meters of fiber. One factor which should be addressed when using fiber optics is the effect of such absorption bands on the measured spectrum. In this application of fiber optic spectrophotometry, the silanol band occurs in the range of wavelengths used for calibration. One effect of this absorption band is the addition of photometric noise due to the decrease in absolute light levels reaching the detector. Since the 112 meters of fiber previously used gave a silanol band with a peak absorbance of approximately 1.1 absorbance units, a shorter run of fiber was selected in an attempt to reduce the peak absorbance of the silanol band. This should improve the signal-to-noise characteristics of the spectra exclusively in the silanol band region, and possibly improve the modeling of MTBE. The samples from the laboratory calibrations were used to determine the SEE and SEP from calibrations with spectra recorded by using 12 meters of fiber optic cable. Figure 6 gives a plot of the actual volume & MTBE against the predicted volume & MTBE from the work done using 12 meters of fiber.

Table 2 gives a summary of the comparison results obtained using 12 and 112 meters of fiber optic cable.

Table 2
Comparison of Results from Different Fiber Distances

Fiber Distance, m	SEE	SEP
12	0.092	0.126
112	0.108	0.121

The 112 meters of fiber optic cable used in this comparison does not appear to limit the modeling of MTBE.

CONCLUSIONS

The statistical results obtained from independently modeling volumetric and gas chromatographic data from several sets of samples indicates that the limiting factor is the uncertainty associated with the currently implemented gas chromatographic method. SONIR spectroscopy with multivariate calibration techniques introduces an accurate and rapid method of monitoring levels of MTBE for production and laboratory purposes. This coupled with the use of long fiber lengths provides remote, intrinsically safe installation of the NIR analyzer (such as control room location), which permits convenient on-line monitoring of MTBE for refineries.

An additional benefit of remote SONIR spectroscopy which is often overlooked is the elimination of sampling problems. In this study a potential sampling problem was highlighted by the gas chromatographic and SONIR results obtained using the duplicate samples. The samples used to evaluate the repeatability of the ASTM and SONIR methods appear to be individuals rather than duplicates. Since sampling is not required with an operational on-line measurement system, this problem would be eliminated. Furthermore, this technique also has potential for regulatory agencies, where the equipment similar to that used in this experiment could be modified for mobile, field monitoring applications.

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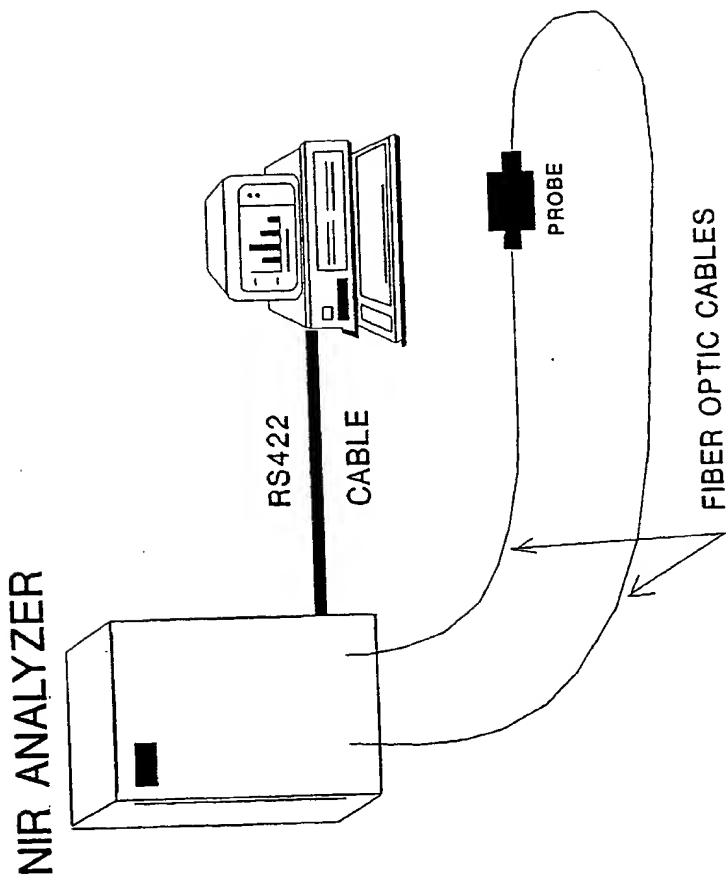


Figure 1: Instrumental system

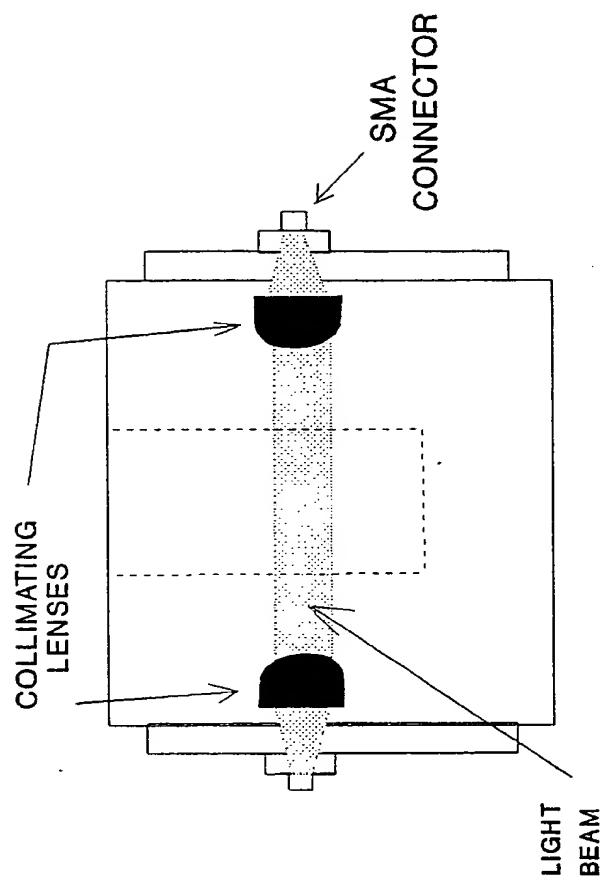


Figure 2: Probe

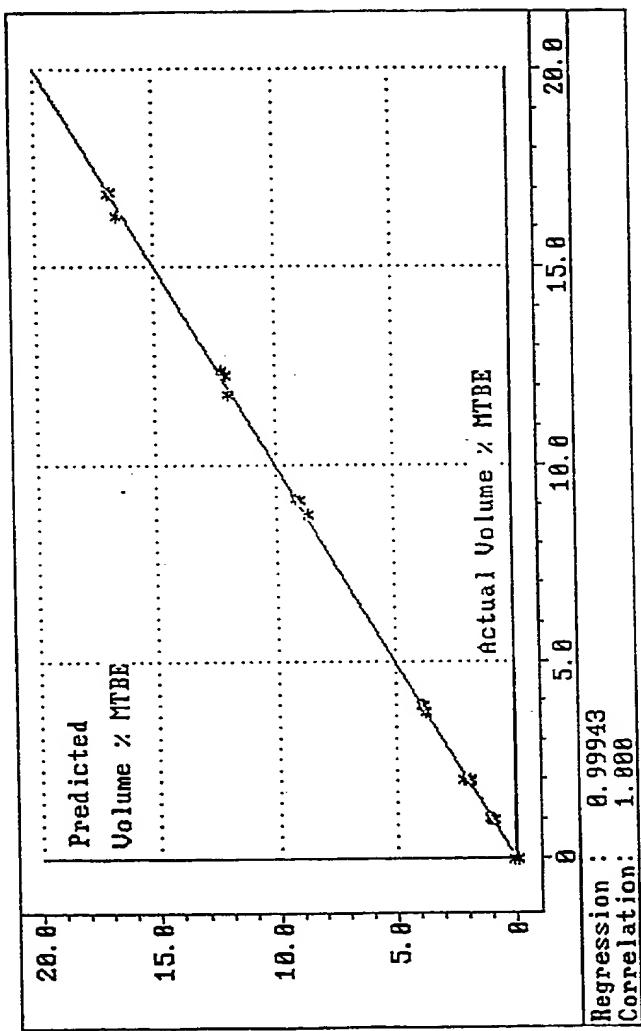


Figure 3

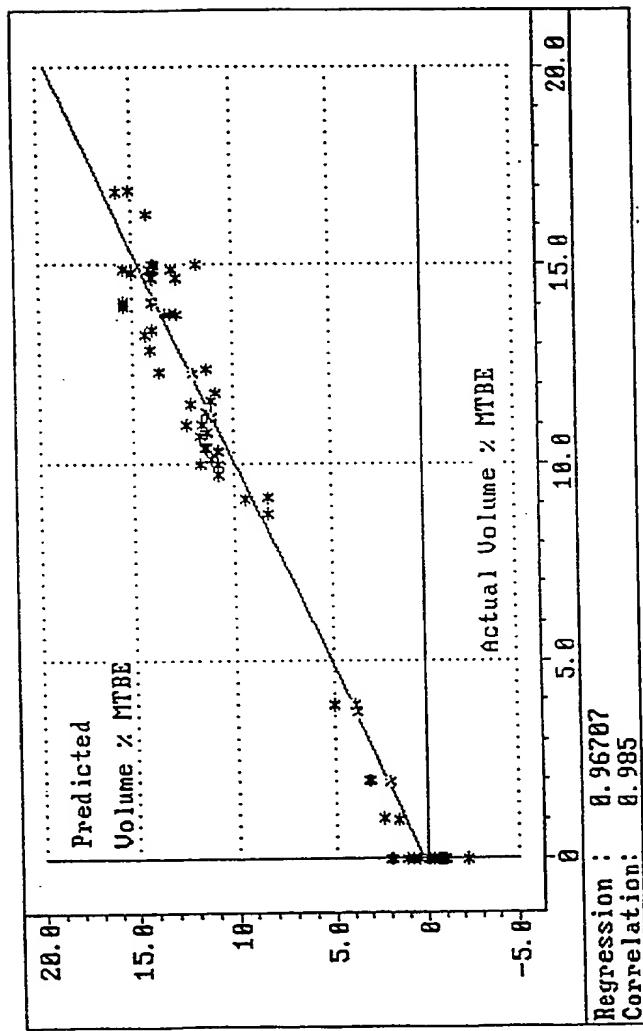


Figure 4

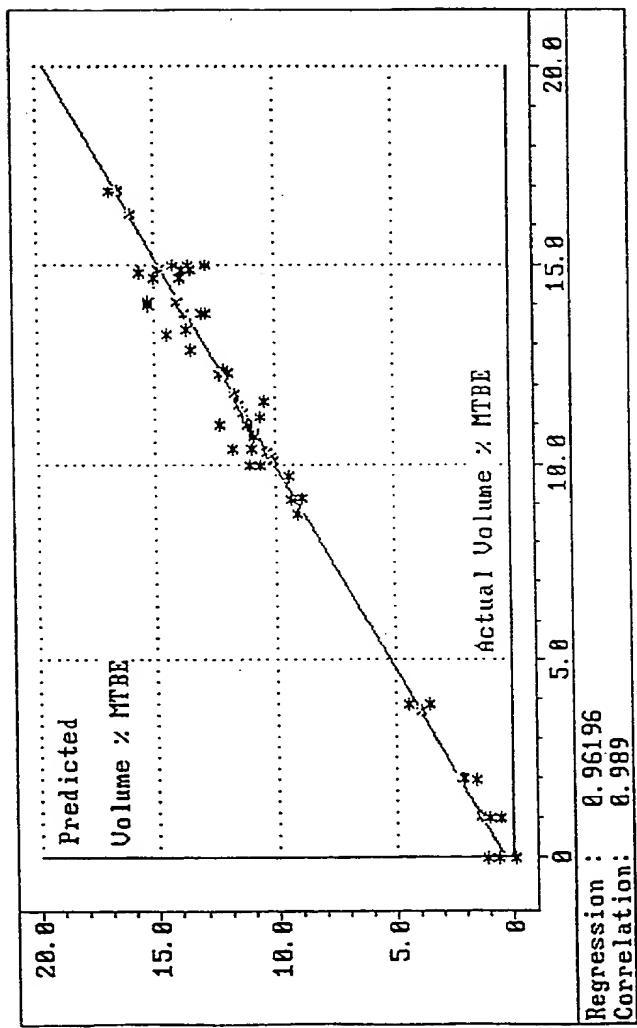


Figure 5

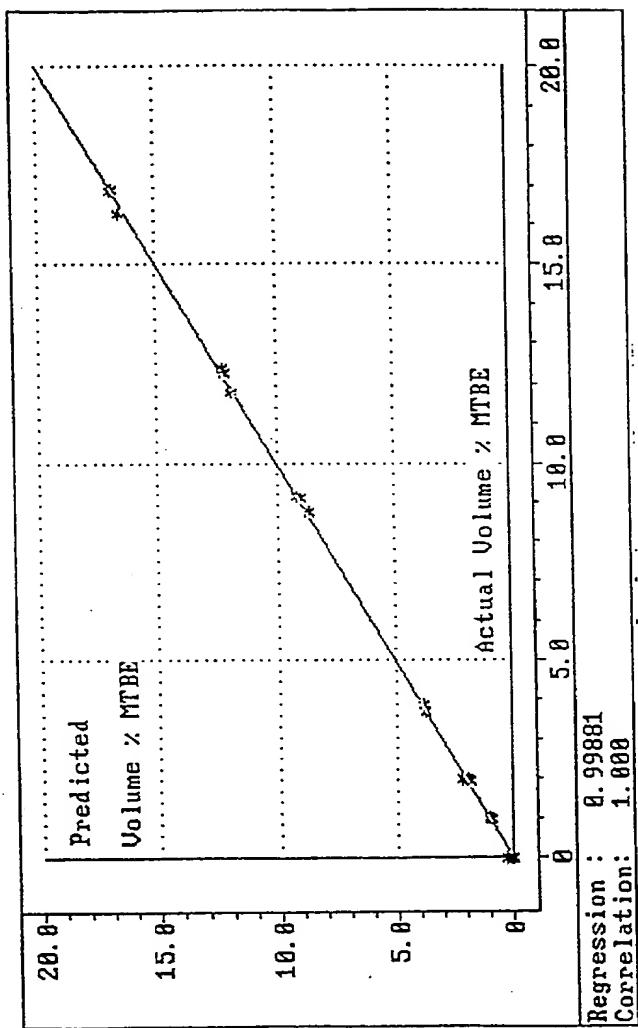


Figure 6

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